SURFACE MODIFICATIONS IN SUPERCRITICAL FLUIDS. APPLICATION TO NEW CORE-SHELL STRUCTURES.

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Abstract

The application of the ICMCB process of nanostructured and nano-materials synthesis by chemical transformation in supercritical fluids is applied to the modification of particle surface. On the one hand, the surface modification can be controlled by organic molecules as in the case of the synthesis of functionalised palladium nanoparticles (7 nm). The organic molecules stabilise the nanoparticles against aggregation and allow to process the palladium nanoparticles in catalysis. On the other hand, the surface modification can be controlled by coating with inorganic compound; the formation of a copper shell at the surface of $SmCo_5$ particles gives access to a new core-shell structure with magnetic properties interesting for magnetic recording.

Introduction

Due to their specific properties, supercritical fluids are more and more used to develop new processes of surface modifications in two main ways: cleaning and coating [1]. The surface cleaning is particularly carried out with supercritical CO_2 in the field of microelectronic industry [2]. This application will be not discussed in this paper which is focused on the surface modification in supercritical fluids by coating.
This coating research activity is mainly developed from the processes of particle production in supercritical fluids. In fact, the well-known processes of materials synthesis in supercritical fluids by a physical transformation or by a chemical transformation were adapted to particle coating and microencapsulation [3 - 5].
In particular, the ICMCB process of materials synthesis in supercritical fluids by chemical transformations is developed to produce new core shell structure materials (Figure 1). Beyond the synthesis of nanostructured materials and nanomaterials with a control of size, morphology and chemical composition, we are working on the control of their surface properties by surface modification. The materials surface can be modified by organic molecules or inorganic compounds to protect, to stabilise, to functionalise, to process, … core of particles. This step of surface modification can be carried out during or after the step of particle synthesis. The control of materials surface properties gives access to the production of new core shell structure materials with specific physical, optical, electronic, chemical, biomedical, … properties.

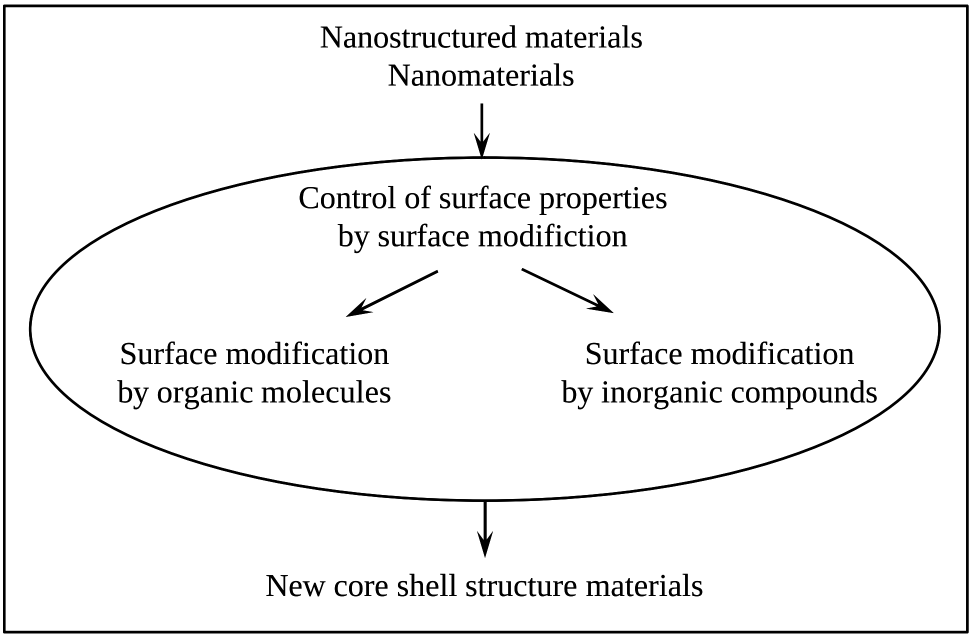

Figure 1: ICMCB process of surface modifications in supercritical fluids

After a description of the ICMCB experimental facilities regarding surface modification in supercritical fluids, the results of two studies are presented: functionalisation of palladium nanoparticles by organic molecules for catalysis and coating of $SmCo_5$ by an inorganic shell for magnetic recording.

I – ICMCB experimental facilities

Three kinds of experimental set-ups are classically used to modify surface in supercritical fluids: a batch experimental set-up with different vessel reactors and two continuous flow facilities, one at a laboratory scale and another at a pilot scale with an in situ analysis by fluorescence spectroscopy. All these facilities are well-described elsewhere [6].

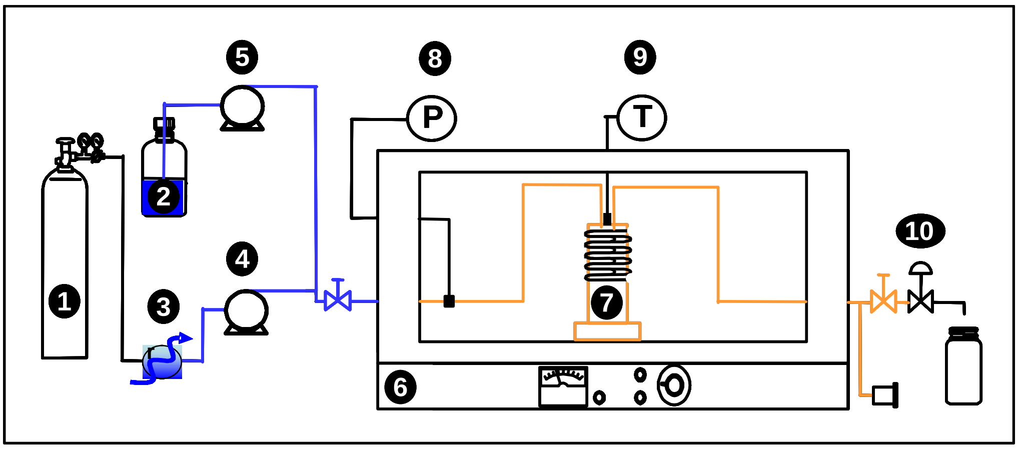

Figure 2: ICMCB experimental set-up of core-shell structure synthesis in batch reactor

In this section, the experimental set-up of core-shell structure synthesis in batch reactor is briefly described; this facility was used to carry out the results presented in the following section (Figure 2). The reactor (7) (possibility of different volumes), placed in an oven (6), is equipped with an external heating resistor and a control of pressure (8) and temperature (9). The facility allows to inject in the reactor the fluid, as instance CO_2, (1, 3, 4) and the reagents (2, 5). After the reactor, there is a line of depressurisation (10).

Beyond the experimental set-ups of synthesis, different characterisation methods are used. The core-shell structures are analysed by microscopy, scanning electron microscopy (SEM, Jeol 840 microscope) and/or by transmission electron microscopy, (TEM, Jeol 2000 FX microscope), by conventional X-Ray Powder Diffraction, XRD (CuKα radiation) and by surface characterisation techniques, as Auger spectroscopy.

II – Hybrid inorganic – organic nanoparticles

The illustration of the control of particle surface properties by surface modification with organic molecules concerns the synthesis of functionalised nanoparticles for catalysis, in particular colloidal catalysis [7]. This new type of catalysis is studied to combine the advantages of homogeneous catalysis in term of activity and selectivity and the advantages of heterogeneous catalysis in term of stability and separability.
Today the challenge is to synthesize nanoparticles of transition metal with a control of the size and of the surface properties.

In this study, the synthesis of functionalised palladium nanoparticles is described. The step of surface modification is carried out during the synthesis.
The experiments were performed in a batch reactor. A solution of palladium acetylacetonate precursor and organic molecules (surface modification agent) in acetone was added in the reactor. Then CO_2 was injected, the reaction media was heated at 100°C and pressurised at 15 MPa and the reduction of the palladium precursor was induced by the addition of hydrogen. After the reactor cooling, a black solution of palladium nanoparticles in acetone was recovered (Figure 3).

a) b)

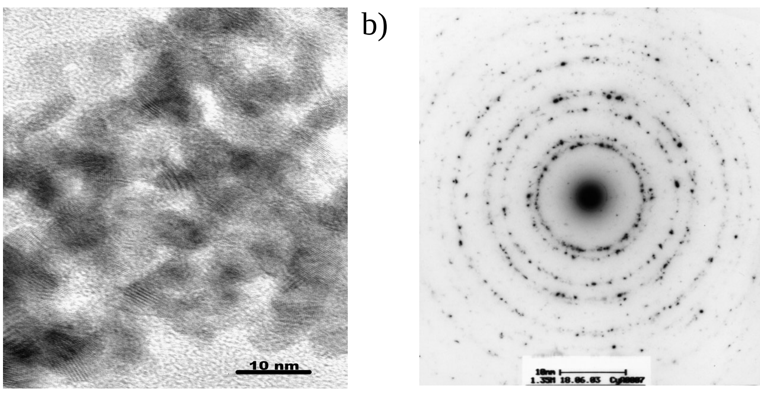

Figure 3: a) TEM picture of functionalised palladium nanoparticles, b) Electron diffraction pattern of these palladium nanoparticles.

Figure 3 shows a TEM picture and an electron diffraction pattern of the synthesised particles. Well-crystallised palladium nanoparticles of about 7 nm were produced. The presence of the organic molecules at the particle surface was confirmed by another experiment performed in the same conditions without organic molecules; bigger particles of a few hundred nanometers were obtained.
The characterisation of the catalytic properties of these functionalised palladium nanoparticles are in progress.

This particular example can be extended to different synthesis of nanomaterials modified at the surface by organic molecules to exhibit specific properties.

III – Inorganic – inorganic core-shell particles

Beyond the surface modification of inorganic nanoparticles by organic molecules, the modification in supercritical fluid of inorganic surface by inorganic compound is equally studied in our laboratory. A process of surface modification in supercritical fluids is developed to coat all types of substrates and, particularly, fine particles (from a few nanometers up to a few micrometers), even with complex morphologies [8]; the process allows to deposit metal, oxide or nitride layers.

New core-shell structures as $SmCo_5$/Cu, for example, were elaborated [9]. $SmCo_5$ exhibits magnetic properties. The coating with an inert shell as copper allows to protect $SmCo_5$ against external attacks. Furthermore, in the magnetic recording field, elementary particles need to be physically small and magnetically independent; so the coating process is a good way in order to get these properties.
The studied $SmCo_5$ particles were prepared by mechanical grinding under argon atmosphere from Sm (99.9%) and Co (99.99%); the particle size is in the range 1 – 10 µm. These particles of $SmCo_5$ were introduced in a batch reactor at the beginning of the reaction. A known amount of copper precursor ($Cu(hfa)_2$) was added to the coating reactor. After a CO_2/ethanol mixture was introduced; the reaction mixture was heated to 130 °C and pressurised to 20 MPa to homogenize the system and to 200 °C and 20 MPa for 15 minutes in order to thermally decompose the copper precursor at the $SmCo_5$ particle surface. At the end of the process, the coated particles are directly recovered free of solvent and organic contamination by depressurisation and cooling.

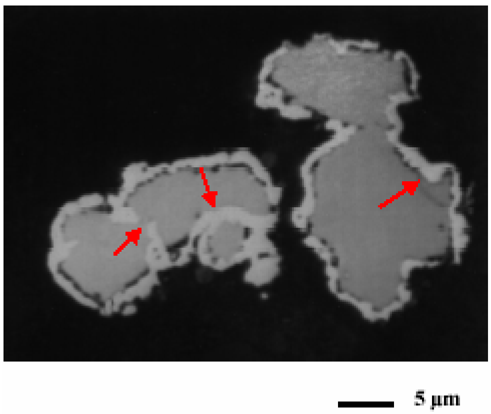

Figure 4: SEM image of a section of $SmCo_5$ particles coated with metal copper

Figure 4 shows a SEM image of a section $SmCo_5$ particles coated with copper. The core particles are uniformly coated with a copper shell. The red arrows indicate the formation of copper into cracks in $SmCo_5$ particles. This leads to the formation of smaller particles which is very interesting in respect with the magnetic properties. Magnetic property analysis of coated $SmCo_5$ particles, made with SQUID (Superconducting Quantum Interference Device) magnetometer, showed a slight decrease in the coercive field, which can be due to the coating together of different randomly magnetically oriented particles.

Conclusions

Different ways of surface modification in supercritical fluids are developed at ICMCB based on our experience in nanostructured and nano-materials synthesis.
Two examples of particle surface modification by organic molecules and inorganic compound are presented.
First, the synthesis of palladium nanoparticles in supercritical fluids in presence of organic molecules gives access to the formation of well-crystallised functionalised palladium nanoparticles (7 nm).
Second, the control of material surface properties by surface modification with inorganic compound is shown with the synthesis of a core-shell structure, $SmCo_5$/Cu, as magnetic particles for information storage.

References

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